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Abstract

It is increasingly recognised that widespread and substantial increases in Dissolved organic carbon (DOC) concentrations in remote surface, and soil, waters in recent decades are linked to declining acid deposition. Effects of rising pH and declining ionic strength on DOC solubility have been proposed as potential dominant mechanisms. However, since DOC in these systems is derived mainly from recently-fixed carbon, and since organic matter decomposition rates are considered sensitive to temperature, uncertainty persists over the extent to which other drivers that could influence DOC production. Such potential drivers include fertilization by nitrogen (N) and global warming. We therefore ran the dynamic soil chemistry model MADOC for a range of UK soils, for which time series data are available, to consider the likely relative importance of decreased deposition of sulphate and chloride, accumulation of reactive N, and higher temperatures, on soil DOC production in different soils. Modelled patterns of DOC change generally agreed favourably with measurements collated over 10-20 years, but differed markedly between sites. While the acidifying effect of sulphur deposition appeared to be the predominant control on the observed soil water DOC trends in all the soils considered other than a blanket peat, the model suggested that over the long term, the effects of nitrogen deposition on N-limited soils may have been sufficient to raise the "acid recovery DOC baseline" significantly. In contrast, reductions in non-marine chloride deposition and effects of long term warming appeared to have been relatively unimportant. The suggestion that future DOC concentrations might exceed preindustrial levels as a consequence of nitrogen pollution has important implications for drinking water catchment management and the setting and pursuit of appropriate restoration targets, but findings still require validation from reliable centennial-scale proxy records, such as those being developed using palaeolimnological techniques.

1. Introduction

Long-term monitoring of surface water quality has revealed increasing concentrations of dissolved organic carbon (DOC) across large parts of the Northern Hemisphere, particularly close to industrialised regions (Skjelkvale et al., 2001, Driscoll et al., 2003, Evans et al., 2005, Monteith et al., 2007, Erlandsson et al., 2008). These observations have raised concerns over increasing water treatment costs (Ritson et al., 2014b) and possible destabilisation of terrestrial carbon stocks (Freeman et al., 2001). A debate has ensued over the possible causes of observed increases (Clark et al., 2010), that have included climate change (Freeman et al., 2001), changes in land management and use (Yallop and Clutterbuck, 2009), nitrogen (N) deposition (Findlay, 2005), CO_2 enrichment (Freeman et al., 2004) and declines in acid deposition (Evans et al., 2006, Monteith et al., 2007). Analyses of surface water data (Evans et al., 2006, de Wit et al., 2007, Oulehle and Hruška, 2009, Erlandsson et al., 2010, Monteith et al., 2014), supported by evidence from laboratory (Clark et al., 2006, Clark et al., 2011) and field studies (Clark et al., 2005, Ekström et al., 2011, Evans et al., 2012) have pointed to effects of declining sulphur deposition as the major cause, but do not exclude the possibility that other drivers have also exerted influence on DOC trends.

Decreases in acid anion concentrations and increases in soil pH associated with a reduction in acid deposition are thought to have increased the solubility of potentially-dissolved organic matter (pDOM) by increasing negative charges on clay and organic matter surfaces (Tipping and Woof, 1991). There is also evidence that regional warming (e.g. Freeman et al., 2001, Pastor et al., 2003) and changes in precipitation patterns (e.g. Keller et al., 2008, Pumpanen et al., 2014) can affect DOC concentrations by influencing decomposition rates, vegetation type or export paths. A further suggested mechanism is the effect of changed flow paths due to changing precipitation patterns (e.g. Hongve et al., 2004, Erlandsson et al., 2008, Couture et al., 2012). The relative degree to which these factors have contributed to DOC trends has been debated extensively (e.g. Evans et al., 2006, Eimers et al., 2008, Futter and de Wit, 2008, Clark et al., 2010).

Several studies suggest that there is also a link between N deposition and DOC leaching (e.g. Pregitzer et al., Findlay, 2005, Bragazza et al., 2006). Nitrogen typically limits productivity in terrestrial ecosystems (Vitousek and Howarth, 1991), so increased net ecosystem productivity due to N deposition might be expected to increase the pool of ecosystem C available for DOC production. This would, however, depend on prevailing levels of ecosystem N saturation. In N-limited ecosystems addition of reactive N would be expected to exert a fertilizing effect (LeBauer and Treseder, 2008). Conversely in N-saturated environments additional N would be expected to contributes to acidification (Emmett et al., 1998), that in turn could reduce decomposition (Janssens et al., 2010), and consequently a reduction in DOC production and solubility (Evans et al., 2008). To predict how DOC levels are likely to change in the future it is therefore necessary to consider the integrated effects of acidifying and eutrophying effects of air pollution and climate change on productivity, decomposition and organic matter dissolution.

One of the criticisms levelled at investigations into the drivers of DOC increases in soils or waters is that studies founded on correlation (e.g. Skjelkvale et al., 2001, Vuorenmaa et al., 2006, Monteith et al., 2007, Oulehle and Hruška, 2009, Sarkkola et al., 2009, Zhang et al., 2010, Borken et al., 2011) do not in themselves provide proof of causation (Roulet and Moore, 2006). In addition, study sites tend to be concentrated within geographically limited areas and findings may, therefore, not necessarily be universally applicable. Furthermore, although soils (particularly upper organic horizons) are recognised to often be the source of most freshwater DOC (e.g. Brooks et al., 1999, Billett et al., 2006, Evans et al., 2007a, Winterdahl et al., 2011), soil water monitoring data are scarce, and typically of shorter duration than surface water data. There is increasing evidence that shallow soil water makes a major contribution to trends in DOC in surface water (Hruška et al., 2014, Sawicka et al., 2016) although the relationship between soil and surface water concentrations is complicated by riparian and subsoil processes (Lofgren et al., 2010, Löfgren and Zetterberg, 2011).

Despite their limitations, however, long-term soil water monitoring data provide the most effective resource for testing whether mechanisms that have been shown to operate in experiments also operate at larger spatial and temporal scales. Therefore, we brought together the United Kingdom's best long term soil solution records in order to provide a foundation for testing our current process understanding and consider how anticipated change in climate and deposition are likely to influence future behaviour of DOC.

To date, the majority of DOC process-based modelling studies have concentrated on model developments and potential applications, or on simulating time series for direct comparison with measurements (e.g. Futter et al., 2007, Futter et al., 2011, Jutras et al., 2011, Xu et al., 2012, Zhang et al., 2013, Dick et al., 2014). Relatively few, in contrast have gone on to consider the longer-term implications of model parameterisation, such as the most likely pre-industrial "baseline" DOC levels that can help to inform catchment restoration and management strategies. Exceptions include, Hruška et al. (2014), who linked a simple empirical DOC function to the MAGIC acidification model to recreate DOC trends in an acid-sensitive podzol site in the Czech Republic. This study was however based on modelling DOC at organo-mineral sites only. Valinia et al. (2015), in turn, reconstructed reference conditions of total organic carbon and long-term monitoring data to predict recent DOC changes in Swedish lakes. Historic reconstructions like these provide a framework with which to consider the likely relative importance of various potential anthropogenic pressures.

In the current study, DOC trends were simulated at long-term monitoring sites using an annual time-step model, with the aim of exploring the likely relative importance of different drivers and considering how DOC concentrations in soil water might be expected to change in the future. Here we use the MADOC model (Rowe et al., 2014) which simulates the long-term controls on DOC from terrestrial sites to streams, is responsive to a number of drivers, and can be applied to catchments at any scale using a lumped-parameter approach. The model is a representation of soil and vegetation carbon dynamics, acid-base dynamics and organic matter dynamics. It has been shown to reproduce the effects of the key drivers of DOC in terrestrial experimental sites and long-term surface water monitoring sites (Rowe et al., 2014). We set out to first test the model directly against soil water monitoring data, and then consider the likely relative effects of key contributory drivers in the model in influencing soil water DOC at a range of sites with different characteristics over the longer term. We therefore applied MADOC to six terrestrial long-term monitoring sites characterised by different vegetation, soil type and acid deposition loading and considered: (1) the extent of discrepancies between modelled trends, based on the hypothesised drivers (anthropogenic sulphate, chloride, N deposition, temperature change), and measured trends and (2) the changes that would have occurred with and without individual drivers to assess the magnitude of impact of each on different ecosystems and on future DOC dynamics.

2. Methods

2.1 Field sites, measurements and chemical analyses

Data from three United Kingdom Forest Level II (FLII) and three terrestrial Environmental Change Network (ECN) sites were used for this study (Figure 1). FLII sites were established in 1995 (Vanguelova et al., 2007) and form part of the European forest monitoring network (ICP Forests) that aims to improve understanding of the effects of air pollution and other environmental factors on forest ecosystem structure, function and health. The monitoring at ECN sites started in 1993 with the objectives of gathering long-term datasets to improve understanding of the causes and consequences of environmental change across a range of semi-natural and agricultural habitats in the UK (ECN, 2014).

Figure 1 Site locations. Triangles indicate Forest Level II monitoring sites (FRLII) and circles indicate Environmental Change Network (ECN) sites.

The FLII sites were composed of stands of Oak (*Quercus robur* and *Q. petraea*) at Grizedale, Scots pine (*Pinus sylvestris*) at Ladybower and Sitka spruce (*Picea sitchensis*) at Llyn Brianne, under standard forest management practices including thinning and brashing during their growth cycle. The forest stands were planted between 1920 and 1974 and cover a range of forest yield classes. The soils were developed from a range of parent materials and include gleysols and podzols (Table 1). The ECN terrestrial sites represent non-forest environments, which are upland grassland (Sourhope) or heathland (Glensaugh) and blanket bog (Moor House) vegetation, subject to seasonal grazing, mainly by sheep. Soil types at the ECN sites include histosols and podzols (Table 1).

The six study sites covered a gradient of S, N and Cl deposition from 44 to 86, 40 to 90, and 94 to 306 meq m^{-2} yr^{-1}, respectively (long-term mean between 1993 and 2010 depending on the site), with a range of soil organic carbon (SOC) content (0.8 to 48.7 %), C/N ratio (3 to 70 g g^{-1}), soil acidity (pH 3.6 to 7.0), and soil sensitivities to acid deposition (e.g. base saturation (BS) 1.1 to 100 %, and Al saturation (Al sat.) 0 to 93.5 %). The sites cover an altitudinal gradient from 115 m to 540 m above sea level. Mean annual temperature (MAT) (for period 2002-2006) varied from 6.1 ^oC at Moor House up to 10.5 ^oC at Ladybower; and mean annual precipitation (MAP) (for 2002-2006) from 1265 mm yr^{-1} at Ladybower to 2020 mm yr^{-1} at Llyn Brianne. Additional information about the monitoring networks is available in Vanguelova et al. (2007) and (Sier and Monteith, 2016).

At FLII sites soil water samples were collected every two weeks using tension lysimeters (PRENART SuperQuartz soil water samplers, Plenart Equipment Aps, Denmark). Twelve lysimeters were installed at each site, six located at 10 cm soil depth and the other six at 50 cm soil depth. Soil water samples were collected and measured according to Level II protocols described in detail in the ICP forests manual (ICP, 2006). Water samples were filtered through a 0.45 µm membrane filter and analysed for pH; total aluminium (Al), calcium (Ca), magnesium (Mg), potassium (K), sodium (Na) and iron (Fe) by ICP-OES (Spectro-flame, Spectro Ltd.); ammonium N (NH_4–N) colorimetrically with sodium salicylate and sodium dichloroisocyanurate; DOC by total carbon analyser (Shimadzu 5000, Osaka, Japan) using catalytic or persulphate oxidation; and sulphate (SO_4), nitrate (NO_3) and chloride (Cl) by Ion Chromatography (Dionex DX-500). Quality assurance and quality control on dissolved ion concentrations in soil water are described by De Vries et al. (2001) and in the ICP manual (2006). ECN soil waters were also sampled fortnightly by tension lysimetry using the same Prenart SuperQuartz samplers. According to the Environmental

Change Network (ECN) protocols six samplers were placed at the base of each A and B horizons, except for deep peats where fixed depths of 10 and 50 cm depths were used. Soil water was analysed for pH, then filtered (<0.45 µm) and analysed for DOC by combustion oxidation and IR (infra-red) gas detection; total metals (Al, Ca, Fe, K, Mg, Na) by ICP-OES; Cl^-, SO_4 by Dionex ion chromatography; and NO_3 colorimetrically with sodium salicylate and sodium dichloroisocyanurate.

At each FLII site, samples from two bulk precipitation (installed in the open ground near the forest plots) and 10 throughfall collectors (installed under the canopy) were collected every two weeks from 1995 until 2006 and precipitation volumes determined by weighing. Water samples were filtered and analysed for the same determinants and by the same methods as soil water samples. Bulk precipitation chemistry was measured at the ECN sites. Samples were collected weekly and were analysed using the same methods for the same determinants as in soil water.

Soils at all FLII and ECN sites were surveyed between 1993 and 1995. In each plot, the soil was described according to the FAO soil classification system and classified according to the World Reference base for soil classification (WRB, 2014). FLII soil sampling and analyses were carried out according to the UNECE ICP Manual for Soil Sampling and Analysis (2006). ECN sites surveys were conducted using standard methods (Sykes and Lane, 1996).

Meteorological data for Grizedale, Ladybower and Llyn Brianne were derived from the nearest Met Office weather stations, within maximum 38km and mean distance of 24km for all sites, available through the British Atmospheric Data Centre (Met Office - MIDAS

Land Surface). Each ECN site has a designated automatic weather station recording hourly climatic data and manual equipment is installed at sites to provide quality control (Morecroft et al., 2009).

2.2 Simulation approach

The MADOC model was developed to simulate long-term changes in carbon and N cycling and soil acidity, and is described fully in Rowe et al. (2014). The model simulates soil processes in a 1-D column, using three annual time-step mechanistic submodels as summarised below (for more details see Supplementary Information). Production and decomposition of organic matter is simulated by the N14C sub-model (Tipping et al., 2012). The model simulates carbon inputs from vegetation productivity, which is determined by temperature, precipitation and N supply. Nitrogen is supplied only from N fixation until the beginning of the industrial period, after which impacts of anthropogenic N deposition are simulated. Nitrogen uptake, immobilization, mineralisation and denitrification processes are included. Decomposition and loss of soil organic matter (SOM) is simulated using conceptual pools with fast, intermediate and slow turnover rates. Most SOM C is lost during turnover as CO_2, with corresponding mineralisation of SOM N to mineral N forms, but a proportion of the calculated turnover enters a 'potentially-dissolved' pool, which may be flocculated/sorbed, or in solution, depending on solution conditions. The solubilisation and dynamics of this pool are calculated using a simplified version of DyDOC (Michalzik et al., 2003). In DyDOC Potentially-dissolved organic matter is partitioned into soluble and solid phases, based on current pH and dilution as determined by net water flux. The solid phase is retained as pDOM and may be solubilised subsequently or lost through mineralisation. The soluble phase (DOC and DON) is leached from the topsoil and mainly enters the freshwater system, although a proportion is sorbed in the subsoil where it is subject to further mineralisation. Acid-base dynamics are simulated using VSD (Posch and Reinds, 2009). In the VSD a constant proportion of DOC is assumed to potentially form acid anions, *i.e.* the dissociation site density, P_{sites}. The actual dissociation of this potential capacity is determined by solution conditions. Simulated soil solution chemistry depends on concentrations of organic anions; nitrate (NO_3) and ammonia (NH_4) inputs as calculated by the N14C model; deposition inputs of the main other acid anions (SO_4 and Cl) and base cations (Na, Ca, Mg and K); and interactions with soil surfaces. Ionic exchange is described by equations that define competition among cations for exchange sites and thus the partitioning of ions between the solution and adsorbed phases.

Since more organic acid anions enter the soil solution when acidity decreases, there is a negative feedback between pH and DOC concentration, and the MADOC model was previously prone to instability when there were abrupt changes in pollutant deposition. The calculation method was improved using a simple second-order integration algorithm, in which the model was first run forward to determine what the organic anion concentration would be assuming no change in pH. The change in pH that this change in anion concentration would result was then calculated. The actual change in soil water pH was assumed to be half of this change, and the actual organic anion concentration was recalculated accordingly. This modification did not change equilibrium values for model outputs, but resulted in considerably faster and more reliable convergence.

Table 1 Sites descriptions. Mean annual temperature (MAT) and precipitation (MAP) are averaged over period of 5 years 2002-2006. World Reference Base (WRB) classification was used to define soil types. Soil properties are given for 10cm depth (depth of the lysimeters placement).

Site name	Network	Soil type (WRB)	Vegetation type	Altitude [m]	MAT [ºC]	MAP [mm]	Acid deposition (Cl + NO_3 + SO_4) [meq m^{-2} y^{-1}]	SOC [%]	C/N	pH	Base Sat. [%]	Al Sat. [%]
Glensaugh	ECN	Podzol	Grassland/ Heathland	300	7.8	1530	263 (158 + 47 + 58)	34.5	28	3.9	5	0.07
Moor House	ECN	Histosol	Blanket bog	540	6.1	1930	209 (125 + 42 + 42)	40.6	32	3.8	11	2.5
Sourhope	ECN	Podzol	Grassland	495	7.7	1280	138 (83 + 21 +35)	48.7	18	3.6	5	0.1
Grizedale	FLII	Podzol	Deciduous forest	115	9.6	1920	423 (317 + 34 + 72)	5.0	17	5.1	7	37.7
Ladybower	FLII	Podzol	Coniferous forest	265	10.5	1265	332 (216 + 46 + 70)	2.7	16	4.1	4	93.5
Llyn Brianne	FLII	Gleysol	Coniferous forest	450	10.1	2020	447 (340 + 31 + 76)	40.1	17	3.6	15	50.9

2.3 Model setup and calibration

2.3.1 Data preparation

Deposition input trajectories (Figure 2) were developed using a combination of modelled, measured and calibrated data. Measured NO_3 and NH_4 deposition was used for the years where it was available (1993-2010 for ECN sites and 1996-2006 for FLII sites). For the previous (from 1850) and subsequent years (including forecasts), modelled sequences from the FRAME model were used (Dore et al., 2009). The pre-industrial level of N input, comprising natural deposition plus N_2 fixation (DeLuca et al., 2008), was set at 0.3 g m^{-2} yr^{-1} (Tipping et al., 2012). Anthropogenic N deposition during the 1850 - 1910 period was assumed to increase linearly from zero to the rate calculated by the deposition model for 1910 (Rowe et al., 2014).

The ‘present day’ was defined as year 2010 and present-day deposition was adjusted for each site to the mean non-marine sulphate ($nmSO_4$) in soil water in 2010 by minimising the error in solution SO_4 using Nelder-Mead algorithm (Nelder and Mead, 1965). Peatlands often retain a proportion of S inputs in reduced organic forms and sulphides (Adamson et al., 2001), and the sulphate retention coefficient (fS_{ret}) for the peatland site included in the study was set to 0.6 on the basis of input-output fluxes. The soils of the remaining (non-peat) sites were assumed not to retain significant amounts of S, and thus fS_{ret} was set to zero. Transport of SO_4 through the soil profile was otherwise assumed to be conservative, and present-day $nmSO_4$ deposition at the site was calculated as that required to produce the observed soil output flux. The long-term $nmSO_4$ deposition sequence was then calculated by scaling the sequence observed at the Eskdalemuir monitoring site for the years 1973 – 2007 (Fowler et al. (2005) to each site specific value. Historic S deposition trajectories (1850-1973) were obtained by scaling estimates obtained using the FRAME model (Dore et al., 2009) to the calculated value for 1973 according to the equation: $Deposition\ Site_{year\ t} = Deposition\ Esk_{year\ t} \cdot \frac{Deposition\ Site_{2010}}{Deposition\ Esk_{2010}}$, where *Deposition Site*$_{2010}$ is calculated by MADOC based on SO_4 concentration in soil water (as above). In order to calculate the total deposition load the dry deposition S trend was assumed to be uniform across the UK and proportional to bulk deposition, as in Fowler et al. (2005).

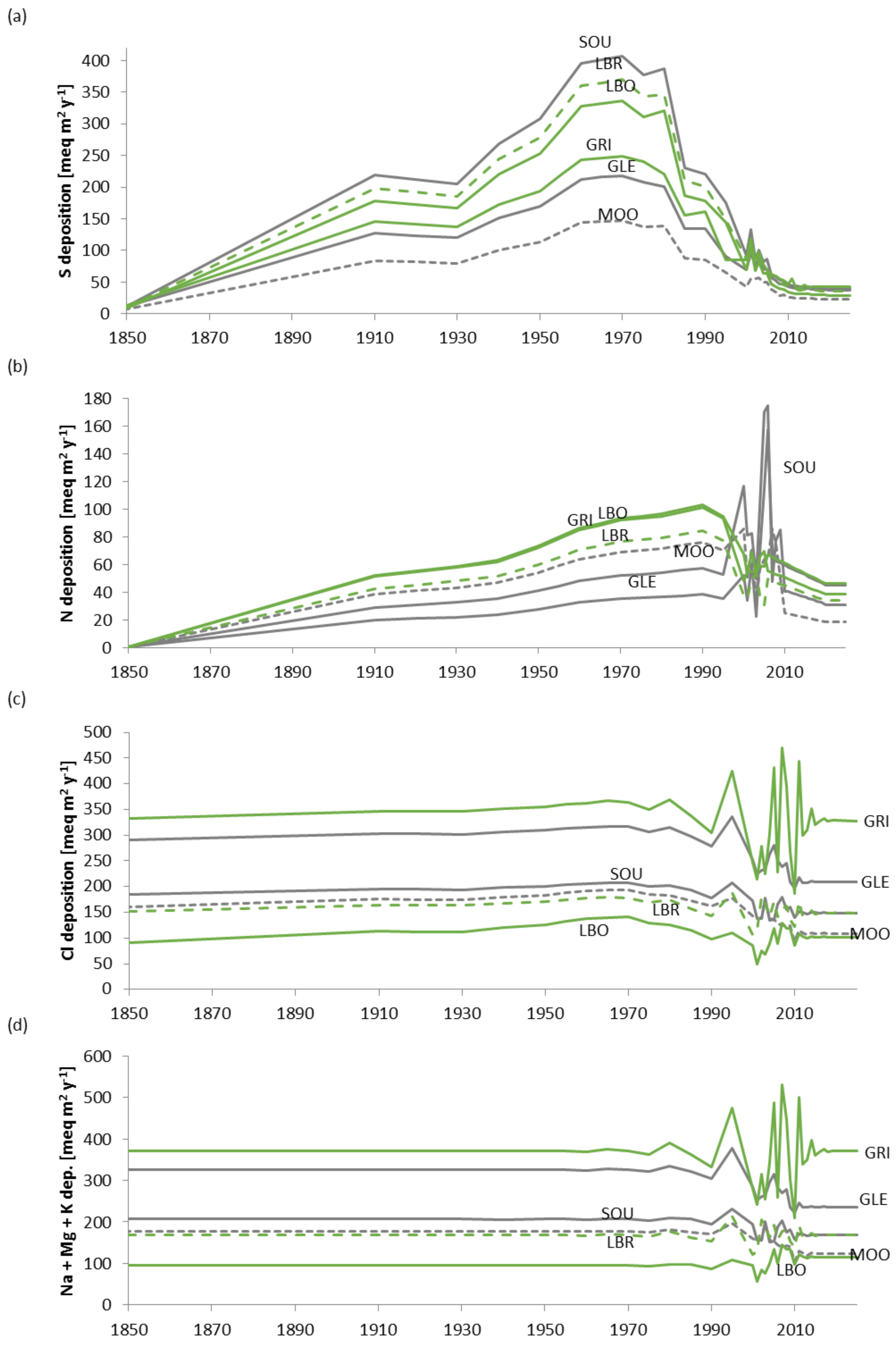


Figure 2 Trajectories of deposition rates for: (a) total nitrogen [meq N m^{-2} y^{-1}], (b) total sulphate [meq S m^{-2} y^{-1}], (c) total chloride [meq Cl m^{-2} y^{-1}], and (d) charge sum of total base cations [meq Na + Ca + Mg + K m^{-2} y^{-1}] for the studied sites. Green colour indicates forested sites and grey colour indicates non-forested sites. Solid line indicates podzol sites, dotted line indicates peat and dashed line indicates gleysol.

To account for anthropogenic Cl deposition, sites were allocated to one of four non-marine Cl (nmCl) regional deposition patterns in geographical zones after Evans et al. (2011). Present day nmCl deposition was assumed to be negligible and linear regression was used to reconstruct preceding annual mean values of nmCl deposition up to year 1986 (the earliest year represented in Evans et al., (2011)). The trajectory of nmCl before year 1986 was assumed to have the same shape as anthropogenic S deposition.

Trends in sea-salt ion deposition, namely the marine fractions of total Cl, Mg, Ca, K and marine SO_4, deposition trajectories, were calculated on the basis of the ratios in which these ions are known to occur with Na in sea salt. Firstly, all Na was assumed to be of marine origin, and ‘present day’ marine inputs of Na^+ were calibrated to soil water concentrations using the implemented solver based on Nelder-Mead algorithm (Nelder and Mead, 1965). Next, Cl deposition was calculated using the marine proportions factor of 1.163 (Evans et al., 2001). If the Cl concentration in soil water was overestimated then Cl deposition was adjusted to correspond to soil water concentrations. This decreased Na deposition (according to sea-salt ratio) and where necessary assumed Na weathering was increased to match soil water Na concentrations. Deposition of other sea-salt cations was then calculated on the basis of the ratios in which these ions are known to occur with Na^+ in sea water (eq eq^{-1}): 0.244 for Mg^{2+}, 0.047 for Ca^{2+}, 0.022 for K^+ and 0.121 for SO_4^{2-}, following Evans et al. (2001).

The mean annual temperature (MAT) trajectory for each site was modelled using a HadCRUT4 (Morice et al., 2012b) mean annual average temperatures for the northern hemisphere from the beginning of the previous century until present (Morice et al., 2012a) fitted to the present-day values.

Inputs for the MADOC model are listed in Table 2 and Table 3. The annual drainage flux, i.e. the water flux flowing down through the soil profile, was assumed to equal annual effective rainfall. Organic acids were assumed to be triprotic, and mean values from a study by Oulehle et al. (2013) were used to set dissociation constants for the three protons. The partial pressure of CO_2 in solution in soil was assumed to be 0.037 atm, i.e. 100 times atmospheric concentration (Rowe et al., 2014). Net base cation uptake was assumed to be zero, except for forested sites where a constant uptake rate was assumed from the initiation of each plantation (Table 4). Weathering of N, Cl and S was assumed to be zero. The temperature range (i.e. the difference between growing season and non-growing season mean temperature) was set to 7^{o}C for all sites. The temperature coefficient Q^{10} was assumed to be 2.0, i.e. decomposition measured in terms of soil respiration (i.e. CO2 loss) doubles for a 10oC increase in temperature (Kätterer et al., 1998, Davidson and Janssens, 2006, Xu et al., 2014). Values for MADOC inputs which are difficult to ascertain empirically were then obtained by calibrating the model to observations, as described below. Values for other input parameters for the N14C sub-model were as described by Tipping et al. (2012).

Table 2 Site-specific inputs for the MADOC model.

Input	Description	Glensaugh	Moor House	Sourhope	Grizedale	Ladybower	Llyn Brianne
k_{Alox}	aluminium equilibrium constant	0.001 [a]	0.001 [a]	0.001 [a]	80.0 [a]	0.01 [a]	0.001 [a]
k_{minpd}	Proportion of potential DOC mineralized, yr^{-1}	0.094 [a]	0.076 [a]	0.049 [a]	0.276 [a]	0.037 [a]	0.133 [a]
k_{inpdC}	Proportion of C turnover entering potentially-dissolved pool	0.172 [a]	0.240 [a]	0.227 [a]	0.145 [a]	0.086 [a]	0.171 [a]
P_{sites}	Dissociable protons per mol DOC, eq(-) mol^{-1}	0.134 [a]	0.130 [a]	0.110 [a]	0.09 [a]	0.110 [a]	0.15 [a]
W_{Na}	weathering rate for Na, meq m^{-3} yr^{-1}	0.614 [a]	0.805 [a]	0.725 [a]	0 [a]	0 [a]	0.31 [a]
W_{BC}	topsoil weathering rate for base cations (Ca^{2+} + Mg^{2+} + K^{+}) meq m^{-3} yr^{-1}	0.197 [a]	0.398 [a]	0.701 [a]	0.891 [a]	0.715 [a]	0 [a]
T_{org}	thickness of organic soil horizon, m	0.10	0.1	0.1	0.02	0.025	0.1
T_{min}	thickness of mineral soil horizon, m	-	-	-	0.08	0.075	-
PPTN	annual precipitation, m	1.532	1.933	1.28	1.92	1.264	2.02
W_d	drainage flux, m yr^{-1}	1.33	1.73	1.07	1.23	0.37	0.92
BD	soil field bulk density, kg dry mass L^{-1}	0.22	0.07	0.24	0.243	0.492	0.434
theta	average annual volumetric water content, m^3 m^{-3}	0.74	0.77	0.79	0.64	0.52	0.77
P_{nit}	nitrate proportion of (nitrate + ammonium)	0.74	0.29	0.262	0.92	0.99	0.88
MAT	mean annual temperature, ^{o}C	7.6	6.1	7.7	9.6	10.5	10.1
Planttype	1=Broadleaf, 2=Conifer,3=Herbs,4=Shrub	4	4	3	1	2	3
CEC	cation exchange capacity, meq kg^{-1}	234.36	498.82	152.28	129.18	65.13	165.36
f_{Sret}	proportion of S deposition retained	0 [a]	0.603 [a]	0 [a]	0 [a]	0 [a]	0 [a]
K_{AlBc}	selectivity constant for Al-Bc exchange	6.3 [b]	8.7 [b]	6.3 [b]	6.3 [b]	6.3 [b]	6.3 [b]
k_{inpdN}	Proportion of N turnover entering potentially-dissolved pool	0.066 [a]	0.09 [a]	0.114 [a]	0.104 [a]	0.03 [a]	-0 [a]

[a] fitted; [b] (Hall et al., 2003);

Table 3 Fixed inputs for the MADOC model.

Input	Description	Value
α_{org}	DOC sorption constant in organic soil, $m^3\ g^{-1}\ L\ mol^{-1}$	6.34×10^{6} [a]
α_{min}	DOC sorption constant in mineral soil, $m^3\ g^{-1}\ L\ mol^{-1}$	6.88×10^{6} [a]
pKpar(1)	1st dissociation constant for triprotic organic acids	3.5 [c]
pKpar(2)	2nd dissociation constant for triprotic organic acids	4.4 [c]
pKpar(3)	3rd dissociation constant for triprotic organic acids	5.5 [c]
K_{HBc}	selectivity constant for H-Bc exchange	199.5 [b]
exp_{Al}	aluminium equilibrium exponent	1.85 [d]
Q_{10}	Rate of decomposition change driven by 10°C temperature increase	2.0 [e]

[a] fitted; [b] Hall et al. (2003); [c](Oulehle et al., 2013), [d] UBA (2004), [e] (Kätterer et al., 1998)

Table 4 Site-specific base cation uptake [meq $m^{-2}\ y^{-1}$] for forested sites included as a flat rate from approximate plantation start.

		Uptake [meq $m^{-2}\ y^{-1}$]		
Site	Plantation start	Ca^{2+}	Mg^{2+}	K^{+}
Grizedale	1900	19.5	3.5	8.5
Ladybower	1952	17.7	5.3	4.0
Llyn Brianne	1965	25.3	6.5	7.9

2.3.2 Calibration of model parameters

The model was calibrated to the measurements made at each site individually. The methodology for the calibration procedure was based on that described by Rowe et al. (2014). The calibration was based on minimizing the sum of absolute differences between observations and predictions using the Nelder-Mead simplex method (Nelder and Mead, 1965). For simultaneous calibrations to more than one type of indicator, indicators were given equal weighting by dividing each error term by the mean measured value. Simulations began 12,000 years before present, to allow organic matter pools simulated by the N14C sub-model to stabilize. Parameter values were fitted in the following sequence: 1) Na^+ and BC weathering rates (W_{Na}, W_{BC}) were calibrated for each site to best predict the concentrations in soil water; 2) the proportion of N entering the potentially-dissolved pool (k_{inpdN}) was calibrated for each site to minimize error in the average C/N ratio in soil above the lysimeters; 3) the proportion of C entering the potentially-dissolved pool (k_{inpdC}) and the mineralization rate (k_{minpd}) were calibrated to best predict DOC concentration; 4) the site density of potentially-dissociated organic acid functional groups on DOC (P_{sites}) (constrained to the range between 0.09 – 0.15 eq mol^{-1}) (Oulehle et al., 2013) was calibrated for each site and soil type to minimize error in soil water pH. Calibration of k_{inpdN} resulted in low or zero values in some cases, illustrating low net N loss at these sites. This low net loss could also be explained by relatively high N fixation or low denitrification, but each of these processes is poorly constrained, so the ki_{npdN} was the only parameter selected for adjustment.

2.3.3 Model performance

The accuracy of DOC predictions was assessed using the absolute error as a proportion of the mean. The statistic should be interpreted as follows: if the calculated value is less than 0.2 the error is less than 20% (i.e. good and comparable to analytical uncertainties [accuracy and precision]). If it is more than 200% the model performs poorly. The patterns and behaviours that were reproduced by the model were also inspected visually.

2.3.4 Pollution and climate scenarios

The scenarios for the historic DOC simulations are listed in Table 5. These were designed to assess the relative impact of four plausible causes of DOC increases. The model was run with (1) combined effect of warming, anthropogenic S, anthropogenic Cl, and N, (2) no anthropogenic forces, (3) anthropogenic warming only, (4) anthropogenic S effect only, (5) anthropogenic Cl effect only, (6) anthropogenic N effect only.

Table 5 Description of scenarios used for analysing alternative DOC trends.

Scenario	Description
1	Combined effect of the selected drivers (S, N, Cl and warming) [a]
2	No anthropogenic force [b]
3	Anthropogenic warming only
4	Anthropogenic S effect only
5	Anthropogenic Cl effect only
6	Anthropogenic N effect only

[a] deposition and temperature trajectories as described in section 2.3 - Model setup and calibration; [b] all deposition and temperature values set to value from 1850 year (presented in section 2.3 - Model setup and calibration) and assumed constant throughout the simulation period.

3. Results

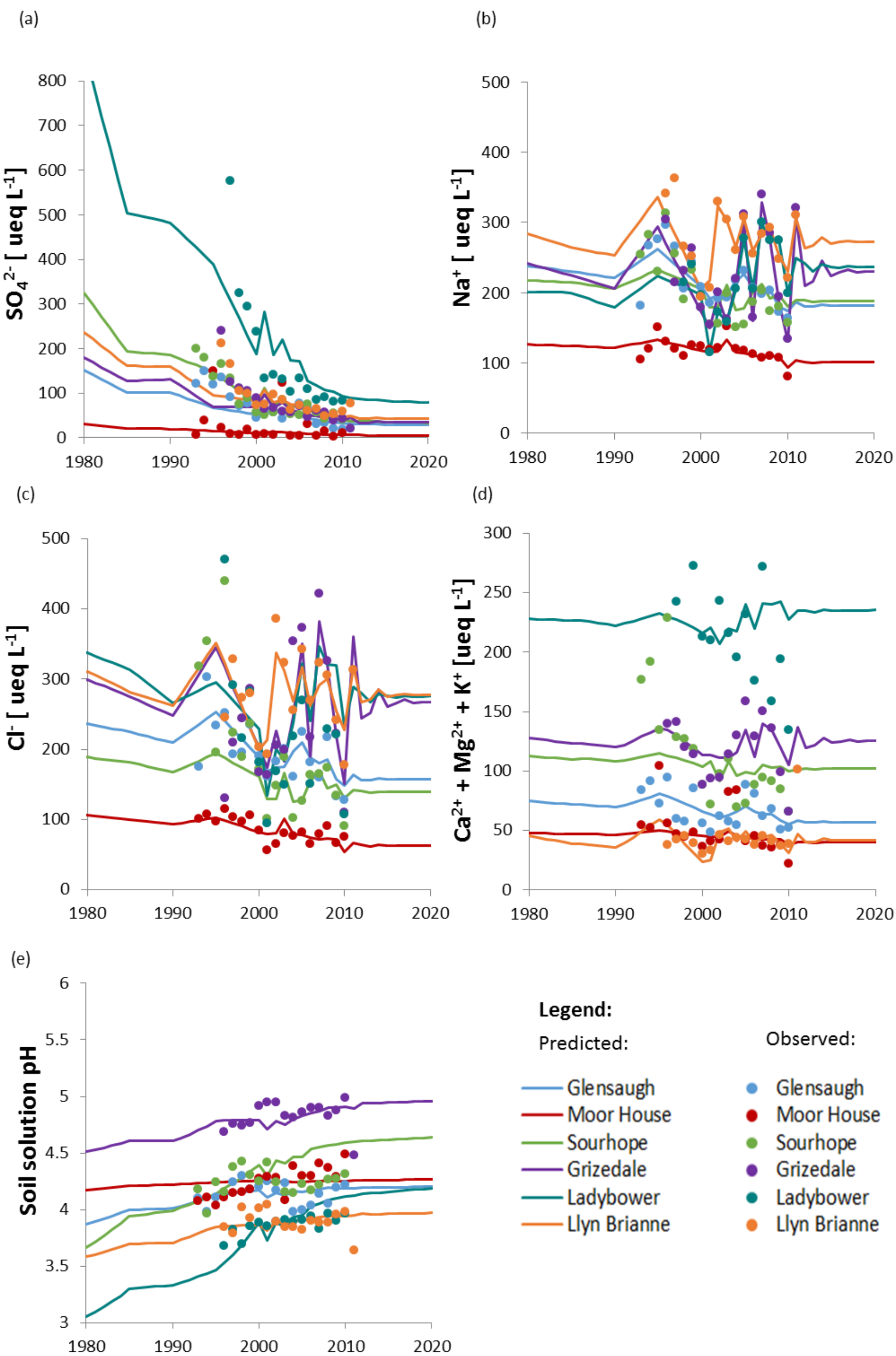
3.1 Major ions in soil solution

Overall, MADOC predictions corresponded well with observed concentrations of major ions (Table 6). Observed declines in soil water SO_4 were reproduced

Table 6 Model performance assessment using the absolute error as a proportion of the mean efficiency criterion for selected soil water indicators concentrations.

Site/Variable	SO_4	Cl	Na	Ca+Mg+K	pH	DOC
Glensaugh	0.27	0.11	0.03	0.16	0.02	0.12
Moor House	0.26	0.10	0.04	0.09	0.03	0.08
Sourhope	0.18	0.12	0.11	0.16	0.04	0.08
Lady Bower	0.23	0.20	0.004	0.16	0.02	0.17
Llyn Brianne	0.13	0.06	0.02	0.15	0.01	0.14
Grizedale	0.22	0.12	0.04	0.11	0.01	0.12

by MADOC (Figure 3a), although at the beginning of the monitoring period SO_4 concentrations were underestimated relative to observations at most sites, suggesting that anthropogenic S deposition was higher at this time than the extrapolated Eskdalemuir bulk deposition sequence would indicate. The model also reproduced the downward trends in Cl concentrations at Glensaugh and Moor House (Figure 3c). Base cation measurements were also mainly predicted accurately (Figure 3d), although the model failed to reproduce the very high base cation concentrations at Sourhope in the early years, again presumably reflecting a discrepancy between the S deposition data used to drive MADOC and higher true S deposition rates. The rate of long-term recovery from acidification was captured well at Llyn Brianne, Grizedale and Glensaugh, slightly over-predicted at Sourhope and Ladybower, and underpredicted at Moor House, where the model failed to reproduce the observed recovery of pH.



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416 **Figure 3 Observed (dots) and predicted (lines) values of selected indicators for the studied sites.**

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3.2 Dissolved organic carbon

The MADOC model reproduced observed long-term changes in DOC concentrations reasonably well for all sites (Figure 4). In five cases the model captured the overall upward trends in the observations more effectively than a line with zero slope, while also simulating the absence of trend in the DOC data for Moor House (Figure 5). The model was not designed to reproduce between-year fluctuations in mean DOC (or other variables) associated with factors such as climate variability (e.g. Clark et al., 2011), so inevitably the predictions fluctuate less than the observations. However, the model reproduced the temporal pattern and rates of DOC change across the sites with most sites showing an upward trend in DOC.

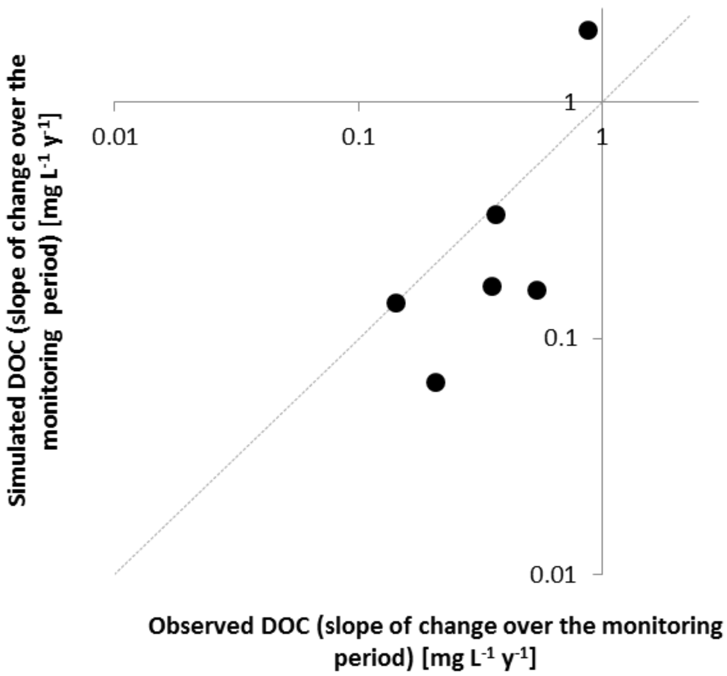

Figure 4 Comparisons of observed with predicted rate of change for the monitoring period for each site DOC concentrations; Equivalence (1:1) lines are also shown. The values are presented on the log-log-scale.

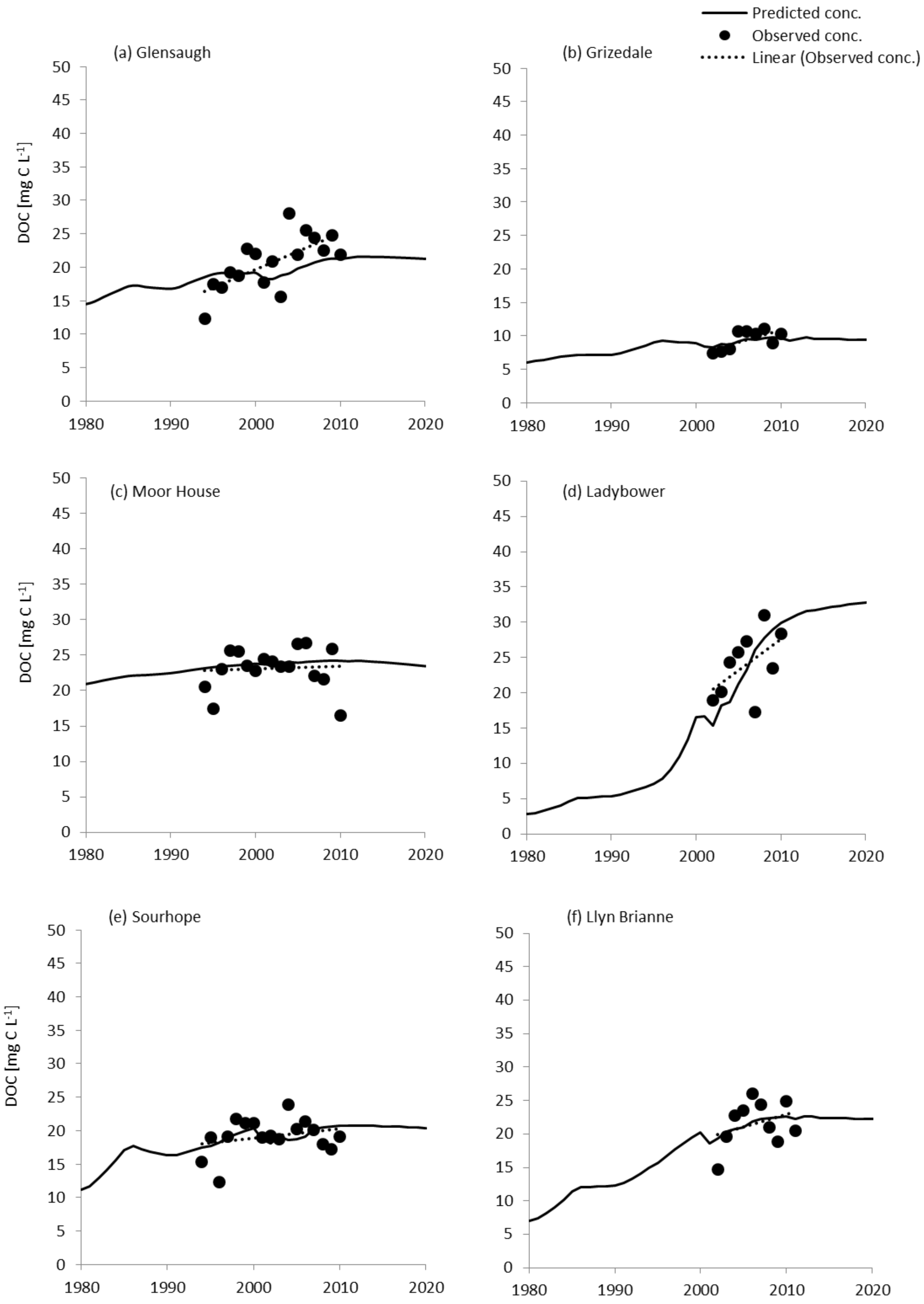

Figure 5 Observed DOC concentrations (dots), fitted linear trend to the observed values (dotted line) and predicted DOC concentrations values by MADOC (solid line) for the studied sites.

3.3 Alternative historical reconstructions of DOC trends

To explore the influence of the main anthropogenic drivers of change within the model, i.e. individual impacts of S, N and Cl deposition and temperature trajectories (Table 5), the calibrated model was applied to each site to simulate long-term DOC trends, first with all four parameters varying according to the historic reconstruction scenarios, and then with all but one fixed. Since a fertilising effect of N deposition for N-limited soils is an implicit assumption in the full model runs, and since the modelled DOC mean for the site is calibrated against measurements on a site specific basis, close fits to observations were only likely to be achieved using the full model or N deposition-only scenarios. Reconstructions under non N-deposition sequences will inevitably under-predict theoretical pre-industrial and current DOC concentrations, where the assumption is that only one driver (e.g. S deposition) is operating. The reconstructions in Figure 6, therefore, need to be interpreted in terms of expected long term change in DOC relative to a common pre-industrial baseline in the case of these different scenarios, and do not provide an indication of theoretical absolute differences between scenarios in hypothetical pre-industrial levels.

With all drivers included, the simulated DOC concentrations for the non-forested podzols (Glensaugh and Sourhope) showed slight decreases until around 1970, before increasing rapidly to levels exceeding pre-industrial reference values (Figure 6a,e). Similarly, at the forested sites (Ladybower, Llyn Brianne and Grizedale) modelled DOC concentrations decreased over the 100 year period following the onset of acidification (Figure 6b,d,f) and increased markedly in the last quarter of the 20th century. Despite a decrease in soil water pH over the 20th century, prior to recovery (not shown), modelled DOC at the peatland site (Moor House) started to increase in early 1900s, reaching a peak after 2000 coincident with the peak in N deposition (Figure 6c).

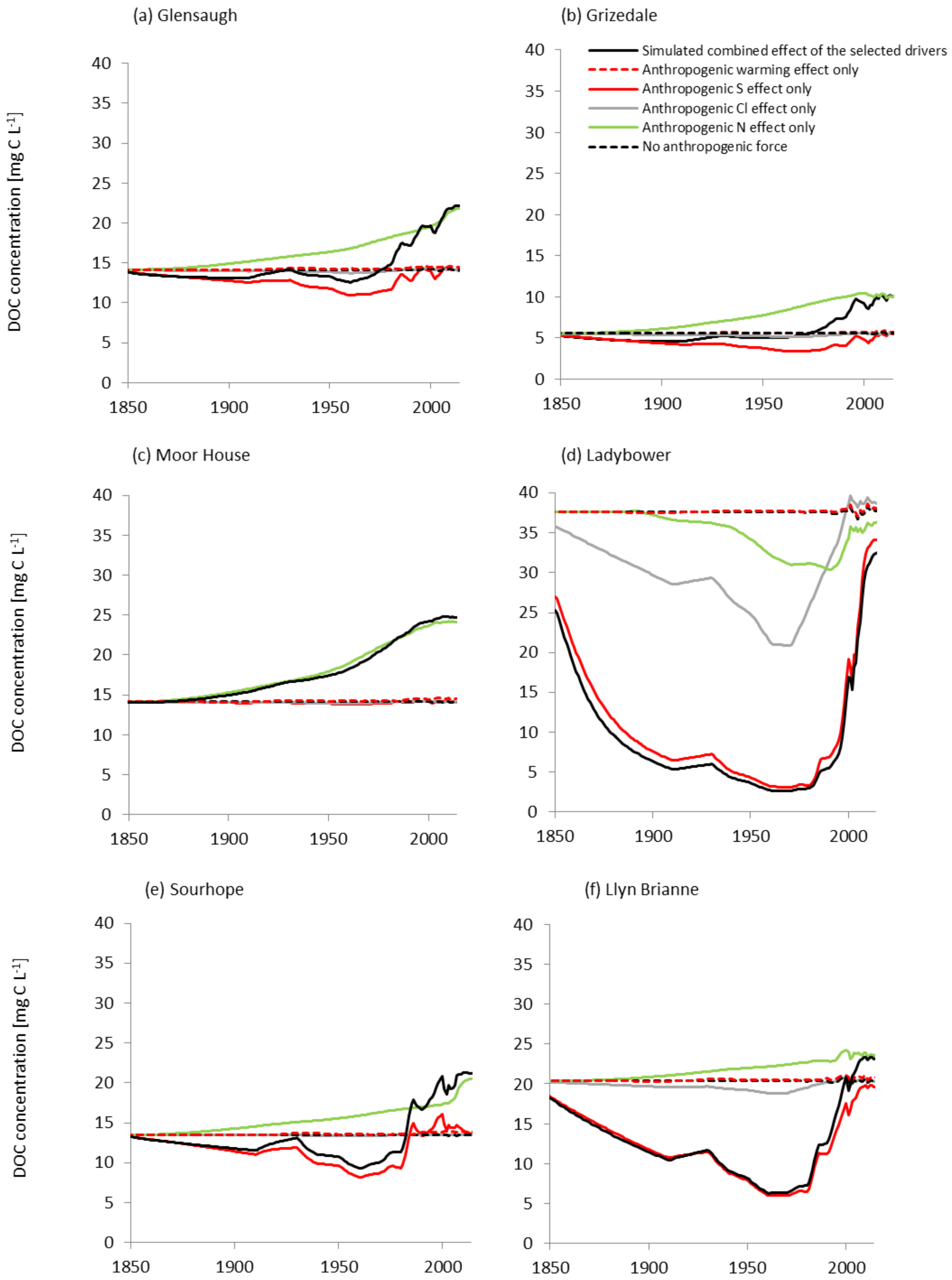

Figure 6 Historic reconstructions of DOC trends under scenarios including actual trends in S, Cl and N deposition and in mean annual temperature (black line), and including each of these trends in isolation: only temperature (dashed red line); only S (solid red line); only Cl (grey line) and only N (green line).

For the S deposition only scenario, modelled DOC variations tracked those in pH with long-term decreases until mid-1990s and recovery onwards, for all sites except Moor House, where negligible change was simulated. The magnitude of simulated DOC change was greatest under conifer forest at Ladybower and Llyn Brianne, reflecting a relatively large soil acidification and recovery response compared to other sites. These scenarios suggest that if recovery from acidification due to S pollution was the only driver of change, present-day DOC concentrations would be close to pre-industrial reference levels. The scenario in which nmCl deposition (another potential acidifying factor) was the only driver of change suggests that nmCl made a negligible contribution to DOC change at most sites, although at Ladybower nmCl deposition alone could have significantly reduced DOC leaching. The simulated impact of this driver was minor compared to that of S deposition.

If N deposition had been the only driver to change with time, the historical reconstruction simulations suggest that there would have been a steady increase in soil water DOC concentrations at all sites other than Ladybower (Figure 6a-c,d,f). In contrast, the conifer site Ladybower showed a decrease in simulated DOC leaching in response to increasing N deposition (Figure 6d). Extremely high NO_3 leaching (over 250 μeq L^{-1} median annual concentration) at this site relative to the others (< 25 μeq L^{-1}, Table 7), implies that N makes a significant contribution to soil water acidity. For all other sites, N deposition would have left current DOC concentrations greatly above pre-industrial levels. For the warming-only scenario, very little variation in DOC concentrations was simulated at any of the sites.

Table 7 Measured annual (2002-2006) median NO_3 concentrations [μeq L^{-1}] in pore water of the topsoil of the studied sites.

Site	Median pore water NO_3 concentrations [μeq L^{-1}]
Glensaugh	2.89
Moor House	0.58
Sourhope	5.22
Grizedale	12.48
Ladybower	254.8
Llyn Brianne	23.38

4. Discussion

4.1 Efficacy of the model in predicting concentrations of soil water indicators

The MADOC model reproduced observations during the monitoring period of major ion concentrations, pH and DOC well at most sites. The reproduction of SO_4 and Cl trends indicates that the model captures adequately the processes governing longer term behaviour of these ions and their annual budgets. The soil water concentrations of sulphate reflected a marked and general decrease in S deposition, a pattern which was also shown in bulk deposition and soil water monitoring data from UK ECN and FLII sites (Sawicka et al., 2016). The underestimation of annual SO_4 concentrations at the beginning of the monitoring period at four sites, and consequent underestimation of effects on pH and DOC concentrations, was presumably because S deposition was underestimated using only nationally wide estimates for dry deposition. The ecosystem type itself strongly influences the deposition process. For example, conifer forest at Ladybower would have had higher levels of scavenged pollutant in comparison to deciduous Grizedale or the non-forested sites (Fowler et al., 1989, Miller et al., 1991) and would also, therefore, have experienced sharper reductions in the deposition load. Given the absence of local dry deposition monitoring at the ECN or FLII sites, the method used generally performed well.

Simulations of Cl concentrations in soil water corresponded well with the monitoring data, and inclusion of the non-marine component estimated from Evans et al. (2011) helped to capture the declining trend in soil water concentrations over the monitoring period. Non-marine Cl has often been overlooked as a driver of ecosystem change, and at polluted sites such as Ladybower the reduction of nmCl deposition could account for up to 40% of chemical recovery from acidification.

Base cation concentrations and trends were reproduced at most sites, although the model did not fully reproduce observed trends at one conifer site (Ladybower) and one grassland site (Sourhope). Historical variation in non-marine inputs of base cations is currently poorly understood, and including base cation deposition trends might improve predictions of soil water concentrations.

Increases in soil water pH with recovery from acidification were reproduced at all sites, albeit with an over-estimation of the rate of pH change under grassland (Sourhope) and conifer (Ladybower) and an under-estimation in peatland (Moor House). The rapid simulated pH recovery in the podzols of Sourhope and Ladybower suggests that increased DOC dissolution with greater pH, which would have buffered the simulated pH increase (Rowe et al., 2014), may be under-represented in the model. The relatively rapid observed increase in pH over the monitoring period at Moor House may be due to an underestimate of nmCl deposition in the late 20th century, and/or to the release of retained reduced S following drought events during the period of intense S pollution.

4.2 Efficacy of the model in predicting DOC concentrations

Despite considerable uncertainties in the driving data, the MADOC model reproduced reasonably well the observed rates of DOC change across different sites (Figure 4). The slow simulated increase in DOC at Glensaugh relative to observations was likely due to underestimation of S inputs in the early part of the monitoring period (see above). Improved estimates of S and base cation deposition sequences would likely improve the accuracy with which DOC observations and trends could be simulated.

Simulated DOC concentrations depended on several factors and processes combined in the model. Modelled DOC concentrations were strongly affected by soil organic matter turnover. Simulated DOC increases over the monitoring period were mostly attributable to the dependence of potentially-dissolved organic matter on pH and therefore on changes in acid deposition and recovery (SanClements et al., 2012, Monteith et al., 2014). However, increased plant productivity due to N fertilisation, and to a lesser extent increased turnover of SOM due to higher temperatures, also affected simulated DOC concentrations at most sites (Figure 6). The importance of SOM turnover in determining DOC concentrations is illustrated by observations that much DOC is of recent origin at least in temperate and boreal systems (Evans et al., 2007a, Raymond et al., 2007, Tipping et al., 2010), although this may not be true for recently drained peats, particularly in the tropics (Evans et al., 2014).

4.3 DOC sensitivity to the elementary drivers.

In general, the agreement between modelled and observed trends was primarily due to the substantial reduction in modelled S deposition and consequent increase in modelled pH. Modelled effects of N deposition at most sites were confined to the pre-monitoring period and are therefore unlikely to explain recent DOC increases at Ladybower, Grizedale, Llyn

Brianne and Sourhope. The simulations therefore suggest that historical changes in soil acidity likely have had a considerably larger effect on DOC concentrations over time than changes in the other potential drivers, and that continuing reductions in sulphur deposition on organo-mineral soils may drive further increases in DOC (Monteith et al., 2015). However this may not be the sole driver of DOC change in all cases, as N deposition alone was able to mimic the recent upward trend at Glensaugh. Nitrogen deposition was the only driver capable of producing a long-term DOC increase in the Moor House peats, although monitoring records do not go back far enough to validate such a trend.

Simulated scenarios with individual drivers demonstrate that the relative effects on DOC fluxes of changes in pH and in productivity are likely to be sensitive to the history of the site in terms of acid and N deposition and on the acid buffering capacity of the soil. At forested sites such as Ladybower with weakly-buffered organo-mineral soils and historically high S interception rates due to canopy effects the model suggests that DOC is likely to be highly sensitive to acidification and recovery, either directly through changing soil acidity (e.g. Vanguelova et al., 2010, Clark et al., 2011, Evans et al., 2012) or via lowered ionic strength (Hruska et al., 2009) and this is borne out between the relatively good agreement between modelled and measured DOC for this site (Figure 5d). By contrast, DOC trends in peatland at Moor House were hardly affected by S deposition, as a consequence of the immobilisation of most S to reduced (and therefore non-acidifying) forms and peats being less sensitive to changes in acidity than organo-mineral soils (Clark et al., 2005, Clark et al., 2011). The model implies that, effects of N on plant productivity and therefore on the turnover of soil organic matter at Moor House, may have been an important driver of DOC historically, in which case current levels may be substantially higher than they were prior to the industrial period.

The reduction in acidity associated with a decline in non-marine Cl deposition has previously been suggested to be a potential driver of slight long-term DOC increases at Moor House (Evans et al., 2011). The MADOC model, in which soil water Cl depends solely on the deposition inputs, reproduced downward trends in annual soil water Cl levels particularly well at the non-forested sites. At historically heavily-polluted sites such as Ladybower, nmCl likely contributed significantly to pH decreases during acidification, and hence recovery from nmCl pollution had a strong influence on subsequent DOC trends. This observation is supported by analysis of long-term monitoring data from ECN and FLII sites (Sawicka et al., 2016). For most sites, however, simulations with and without nmCl forcing were only marginally different, suggesting that nmCl input made only a small contribution to DOC increases. Sawicka et al. (2016) suggested that, rather than industrially derived Cl, it could be that longer term retention and release of Cl from organic complexes (Bastviken et al., 2006) has driven decreases in soil water Cl. Deposition of nmCl can contribute to DOC trends, but at most sites its impact is probably negligible.

The model simulations indicated that the DOC response to the observed historic trend in global temperature may be also negligible. Decomposition rates increase exponentially with temperature, with a Q_{10} here assumed to be 2.0, i.e. decomposition measured in terms of soil respiration (i.e. CO_2 loss) doubles for a 10^{o}C increase in temperature (Kätterer et al., 1998, Davidson and Janssens, 2006, Xu et al., 2014). At such a rate, the simulated increase in DOC due to the 0.66^{o}C increase over the last three decades of the 20th century would have only amounted to a change of 10-20%, suggesting temperature was not a major driver of DOC increase in recent decades (*cf.* Clark et al., 2005, Evans et al., 2006). However, effects of temperature on DOC (via increased plant productivity and increased decomposition rates) are likely to become more significant in future (Futter et al., 2009). This is also consistent with a comprehensive study of climate change impact on DOC in Irish catchments (Naden et al., 2010), which showed that under IPCC future temperature change scenarios DOC concentrations may increase between 20 and 89%.

The MADOC model simulations demonstrate that, according to our current system understanding, current soil water (and hence surface water) DOC concentrations may have been influenced by the long term effects of N deposition and accumulation. On this basis, the pattern of increasing DOC association with recovery from acidification may have obscured a more gradual long-term increase in DOC linked to rising productivity and litter production, with the exception of N-saturated sites such as Ladybower where high NO_3 leaching is likely to have contributed to acidification. Nitrogen fertilising impact will depend on the amount of N input and the degree of limitation by other factors. Low to moderate N deposition to N-limited forests typically stimulates plant growth (Quinn et al., 2010) through positive effects on photosynthesis, and this is supported by modelling and experimental results suggesting increased rates of biomass C sequestration in response to N additions (Holland et al., 1997, de Vries et al., 2009). At N deposition rates above 10 kg N ha^{-1} y^{-1} the growth response of trees to N may become saturated (Fleischer et al., 2013, de Vries et al., 2014) such that litterfall may be unchanged or even decreased under severe N saturation conditions (Aber et al., 1998) due to nutrient imbalances and increased susceptibility to insect attack (Flückiger and Braun, 1998, Kennedy, 2003).

With regard to DOC, the effects of N depostion may also vary, from increased DOC production where additional N stimulates NPP, to decreased production if excess N causes ecological damage or reduced solubility if high NO_3 leaching causes acidification.

Application of the MAGIC dynamic model predicts that in the long-term, despite the recovery of the coniferous sites, there will be re-acidification of sites such as Ladybower if N deposition continues at current rates (Evans et al., 2007b). The ongoing N-enrichment of unforested ecosystems also has the potential to trigger shifts in vegetation communities (Aerts and Berendse, 1988), potentially from plant species adapted to low-N conditions (such as Sphagnum moss and dwarf shrubs), towards more productive species which may alter the proportion of DOC produced relative to NPP and litter quality (Armstrong et al., 2012, Ritson et al., 2014a). There is no evidence that such changes in vegetation have occurred at the sites we have studied during the period of which we have, however it is possible in the future that N-induced plant species changes could provide a negative feedback on the NPP-DOC link over longer time periods (e.g. Chambers et al., 2013). In addition, it is possible that the link between N deposition and NPP will weaken if the ecosystem reaches N saturation, as other limitations to plant growth may then start to dominate, such as temperature, drought, waterlogging (in peaty soils) and deficiency of other nutrients such as phosphorus.

5. Conclusions

The MADOC model was able to reproduce changes in soil water DOC concentrations observed for a range of upland organic soil types, although performance was strongly dependent on deposition sequences, implying that good deposition estimates are essential for site-scale modelling. The application of MADOC to terrestrial monitoring data provides insight into the extent to which drivers other than sulphur deposition might contribute to DOC trends. According to the process understanding and parameterisation we have incorporated in the model, S deposition is likely to have exerted a considerably larger influence on DOC than other potential drivers in most sites. Temperature changes appeared to have had little impact. The relative importance of S and N loading depended on soil sensitivity to acidification, and on N limitation. In all N-limited podzols and gleysols investigated, modelled DOC increases over the monitoring period were dominated by the effects of recovery from acidification (higher DOC solubility), but effects of N enrichment driving higher DOC production may have been important in the longer term. At the most N saturated forest site, it is likely that nitrate leaching will actually have contributed to acidification and reduced DOC leaching, whereas at a peatland site where S deposition was retained through sulphate reduction, N enrichment was the only driver capable of driving a potential DOC change before the monitoring period.

Our modelling study emphasises the possibility that although recent soil and surface water trends in DOC concentrations are keeping up with a return toward pre-industrial levels, concentrations for a range of soil types may now be higher than historical levels as a consequence of the effect of N fertilisation raising the baseline. However, even the longest reliable soil water DOC records only extend back for two decades or so and this is not sufficient to fully disentangle possible acidification recovery and eutrophication effects. Hence further evidence may be best derived through the further refinement of paleolimnological reconstruction approaches that may allow changes in DOC in surface waters to be inferred over centennial time scales, and continued monitoring over an extended period of sulphur deposition rates that now appear to be approaching pre-industrial levels in some areas.

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